

# PATENT ABSTRACTS OF JAPAN

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(54) THERMALLY SHRINKABLE POLYESTER-BASED FILM ROLL AND METHOD  
FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thermally shrinkable polyester-based film roll in which the variations of the thermal shrinkage behaviors of the long film wound on the film roll are reduced, and to provide a method for producing the same.

SOLUTION: This film roll produced by winding up the thermally shrinkable polyester-based film is characterized in that the average value of the maximum shrinkage direction thermal shrinkage rates of samples prepared by cutting the thermally shrinkable polyester-based film at an approximately equal distance in the longitudinal direction is  $\geq 75\%$ , when immersing the samples in 85° C hot water for 10 seconds and then pulling up the samples, and the thermal shrinkage rates of all the samples are within a range of  $\pm 5\%$  of the average thermal shrinkage rate.

## CLAIMS

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[Claim(s)]

[Claim 1]

A heat contraction nature polyester system film roll with which it is a film roll which

rolls round a heat contraction nature polyester system film, and this heat contraction nature polyester system film is characterized by satisfying following requirement (A) – (C).

(A) When an end by the side of a cut water of a film of a constant region whose film properties are stable in the length direction of the above-mentioned film is rolled the 1st end and an end by the side of the end is used as the 2nd end, Less than 2 m inside the 2nd end of the above, provide the last logging part less than 2 m inside the 1st end of the above, and again the 1st sample logging part. A sample logging part is provided every about 100 m from the 1st sample logging part, Average value of a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 70 \*\* warm water, and it pulled up about a sample started 10 cm x 10 cm in the shape of a square, respectively, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up is 10 to 50%,

(B) About each sample of the shape of a square (10 cm x 10 cm) separately started from each sample logging part in requirements (A). Average value of a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 85 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up is not less than 75%, and said heat shrinkage rate of all the samples is settled in less than \*\*5% of range of said average heat shrinkage rate,

(C) Each sample of the shape of a square (10 cm x 10 cm) separately started from each sample logging part in requirements (A), About each sample cut off 10 cm x 10 cm in the shape of a square after making a maximum shrinkage direction carry out heat contraction of the piece of logging of the shape of a square (25 cm x 25 cm) separately started from each sample logging part in requirements (A) 10%. When making into  $X_0$  (%) and  $X_{10}$  (%) a heat shrinkage rate of a maximum shrinkage direction measured when it was immersed for 5 seconds into 95 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up, respectively, The heat shrinkage rate difference delta (%) shown by a lower formula in all the sample logging parts is settled in 10 to 20% of range.

$$\text{delta} = X_0 - X_{10}$$

[Claim 2]

The heat contraction nature polyester system film roll according to claim 1 which is what is formed from a polyester mixture in which two or more sorts of presentations of the above-mentioned heat contraction nature polyester system film differ.

[Claim 3]

0.2 m or more in width, the heat contraction nature polyester system film roll according to claim 1 or 2 with which a heat contraction nature polyester system film not less than 300 m in length is rolled round.

[Claim 4]

Most polyester of the amount used and this polyester are how to manufacture the heat contraction nature polyester system film roll according to any one of claims 1 to 3 including a process of mixing and carrying out melting extrusion of one or more sorts of other polyester in which presentations differ,

It is considered as an elliptic cylindrical shape which has an ellipse section which has a major axis and a minor axis for shape of a raw material chip of each polyester used, A raw material chip of polyester other than most polyester of the amount used, As opposed to a diameter of average length (mm), an average minor axis (mm), and average chip length (mm) of a raw material chip of the amount used, [ of most polyester ] A manufacturing method of a heat contraction nature polyester system film roll considering it as a thing of a diameter of average length (mm) and an average minor axis (mm) which are contained in less than \*\*20% of range, respectively, and average chip length (mm).

[Claim 5]

A manufacturing method of the heat contraction nature polyester system film roll according to claim 4 in which the angle of inclination is a thing using a not less than 65-degree hopper as said hopper including a process of carrying out melting extrusion of the film using an extrusion machine provided with a funnel-like hopper as a raw material chip feed zone.

[Claim 6]

The heat contraction nature polyester system film roll according to claim 5 which is a thing using a hopper which has the capacity of 15 – 120 mass % of discharge quantity per hour of an extrusion machine as the above-mentioned hopper.

[Claim 7]

Once rolling round a film produced by cooling raw material polyester after melting extrusion, Or the range of fluctuation of skin temperature of a film successively measured including a process to extend with an optional point in each of a preheating process, a stretching process, and a heat treatment process after extension after cooling, A manufacturing method of the heat contraction nature polyester system film roll according to any one of claims 4 to 6 which is what covers a film overall length and is controlled to within the limits with a mean temperature of \*\*1 \*\*.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the film roll which rolls round a heat contraction nature polyester system film. It is related with the roll around which the heat contraction nature polyester system film which covers a film overall length substantially in more detail, and shows the uniform heat contraction characteristic was wound. As for the heat contraction nature polyester system film currently rolled round by this roll, little [ and ] poor generating of the shortage of contraction in a contraction work process, contraction spots, a white blush mark, wrinkles, distortion, TATEHIKE, etc. also has very little poor generating by the manufacturing process of a label, a bag, etc.

[Background of the Invention]

[0002]

From the former, a heat contraction nature polyester system film (it may only be hereafter called a "film")., It is widely used for the purpose, such as a contraction (accumulation) package, a shrink label, and a cap seal, for various containers, such as a polyethylene terephthalate (PET) container, a polyethylene container, and glassware, using the character contracted with heating (for example, patent documents 1).

[0003]

In order to manufacture a label etc., the following methods are usually adopted. That is, melt extruding and an unstretched film are continuously manufactured for raw material polyester. Subsequently, it extends and a heat contraction nature polyester system film roll is obtained. Letting out a film from this roll, a slit is carried out to request width and it winds around rolled form again. Then, text and patterns, such as various product names, are printed. By solvent bonding or other means, after the end of printing piles up the right-and-left-ends part of a film, joins, and manufactures a tube (tubing process). A slit process and presswork may have a reverse order. If the obtained tube is suitably cut out to length, it will become a cylindrical label, and a bag can be manufactured if one opening of this cylindrical label is joined.

[0004]

And the contraction tunnel (steam tunnel) of the type which puts the above-mentioned label, a bag, etc. on a container and to which heat contraction of the steam is sprayed and carried out, By spraying a hot wind, putting the inside of the contraction tunnel (hot wind tunnel) of the type which carries out heat contraction on

a band conveyor etc., passing it, and carrying out heat contraction of a label, the bag, etc., it was made to stick to a container and the final product (labeling container) has been obtained.

[0005]

By the way, in this heat contraction process, when change of one-piece one heat shrinkage rates, such as a label and a bag, is large, since the heating conditions in a tunnel are the same, it may be generated by a label, a bag, etc. in which a proper heat shrinkage rate is not shown. In order to cause the appearance defect by distortion of the shortage of contraction, contraction spots, wrinkles, and a pattern, TATEHIKE, etc., it becomes inferior goods and it becomes impossible as a result, to ship to a commercial scene. Usually, since the same label for final products, the bag, etc. were processed from one film roll, when changing sharply the heat contraction action of the film wound around one film roll, there was a problem on which the defective fraction in a heat contraction process increases.

[0006]

In these days, from a viewpoint of recycling, use of an on the other hand especially colored PET bottle follows on being restricted, it replaces with coloring of the bottle itself, and the demand (what is called a full label use) of a wrap is also growing with the label made from a heat contraction nature polyester system film in the great portion of bottle side. However, the side shape of a PET bottle is various, and since an outer diameter changes in arbitrary height positions, the grades of contraction that at least one label which covers the bottle whose number is one is required differ in the height position of a bottle. For this reason, even when it has conventionally better shrink characteristics than elegance and is used for covering of the bottle of complicated side shape, the heat contraction nature polyester system film which can demonstrate the outstanding contraction result nature is called for.

[0007]

For example, with the PET bottle of the bevel use, the case where label wearing and contraction are performed all over a drink charging line is increasing for the productivity drive. Since such a charging line is a high speed, wearing and contraction of a label also become high-speed, and is in the tendency for contraction to be performed for a short time. Therefore, the physical properties which can be equal to high-speed wearing, and the contraction performance which serves as high contraction for a short time are needed for the heat contraction nature polyester system film.

[0008]

In addition, these days, the operation which reinforces these containers is also being expected from the label used for various containers, such as a PET bottle. However, the label obtained from the conventional heat contraction nature polyester system film cannot satisfy such a reinforcing operation.

[Patent documents 1] JP,H7-138388,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0009]

In this invention, a heat contraction nature label, a bag, etc. are manufactured from the roll around which the long film was wound, Put these on a container, carry out heat contraction, and are in charge of providing a labeling container product, By losing dispersion in the heat contraction characteristic of a long film, many problems that it can set at each above process are solved, and let it be SUBJECT to provide a heat contraction nature polyester system film roll which can reduce generating of inferior goods, and a manufacturing method for the same.

[Means for Solving the Problem]

[0010]

This invention is a film roll which rolls round a heat contraction nature polyester system film, and this heat contraction nature polyester system film has a gist at a place with which it is satisfied of following requirement (A) – (C).

(A) When an end by the side of a cut water of a film of a constant region whose film properties are stable in the length direction of the above-mentioned film is rolled the 1st end and an end by the side of the end is used as the 2nd end, Less than 2 m inside the 2nd end of the above, provide the last logging part less than 2 m inside the 1st end of the above, and again the 1st sample logging part. A sample logging part is provided every about 100 m from the 1st sample logging part, Average value of a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 70 \*\* warm water, and it pulled up about a sample started 10 cm x 10 cm in the shape of a square, respectively, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up is 10 to 50%,

(B) About each sample of the shape of a square (10 cm x 10 cm) separately started from each sample logging part in requirements (A). Average value of a heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 85 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up is not less than 75%, and said heat shrinkage rate of all the samples is settled in less than \*\*5% of range of said average heat shrinkage

rate,

(C) Each sample of the shape of a square (10 cm x 10 cm) separately started from each sample logging part in requirements (A), About each sample cut off 10 cm x 10 cm in the shape of a square after making a maximum shrinkage direction carry out heat contraction of the piece of logging of the shape of a square (25 cm x 25 cm) separately started from each sample logging part in requirements (A) 10%. When making into  $X_0$  (%) and  $X_{10}$  (%) a heat shrinkage rate of a maximum shrinkage direction measured when it was immersed for 5 seconds into 95 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up, respectively, The heat shrinkage rate difference delta (%) shown by a lower formula in all the sample logging parts is settled in 10 to 20% of range.

$$\text{delta} = X_0 - X_{10}$$

[0011]

As for a film currently wound around a roll of this invention, it is preferred that it is what is formed from a polyester mixture in which two or more sorts of presentations differ. It is preferred that a heat contraction nature polyester system film 0.2 m or more in width and not less than 300 m in length is rolled round. It is because there is meaning which a film presentation and change of a heat contraction action take place easily, and applies this invention if this invention is not applied even if it mixes polyester in which two or more sorts of presentations differ when manufacturing a film, or when manufacturing a film which has the above-mentioned width and length.

[0012]

It is the method of manufacturing a heat contraction nature polyester system film roll including a process which a manufacturing method of this invention mixes one or more sorts of other polyester in which a presentation differs between most polyester of the amount used, and this polyester, and carries out melting extrusion, It is considered as an elliptic cylindrical shape which has an ellipse section which has a major axis and a minor axis for shape of a raw material chip of each polyester used, A raw material chip of polyester other than most polyester of the amount used, It has a gist at a place made into a diameter of average length (mm), an average minor axis (mm), and average chip length (mm) which are contained in less than \*\*20% of range, respectively to a diameter of average length (mm), an average minor axis (mm), and average chip length (mm) of a raw material chip of the amount used. [ of most polyester ] It is effective for change control of a film presentation.

[0013]

In the above-mentioned manufacturing method, when it includes a process of carrying

out melting extrusion of the film using an extrusion machine provided with a funnel-like hopper as a raw material chip feed zone, it is preferred as the above-mentioned hopper that the angle of inclination uses a not less than 65-degree hopper. It is also effective for change control of a film presentation to use a hopper which has the capacity of 15 – 120 mass % of discharge quantity per hour of an extrusion machine.

[0014]

Once rolling round a film produced by cooling raw material polyester after melting extrusion, Or when it includes a process to extend succeedingly after cooling, it is desirable to cover a film overall length and to control the range of fluctuation of skin temperature of a film measured with an optional point in each of a preheating process, a stretching process, and a heat treatment process after extension to within the limits with a mean temperature of \*\*1 \*\*.

[Effect of the Invention]

[0015]

The heat contraction nature polyester system film roll of this invention covers the constant region overall length of a film, and since change of the heat contraction action of a film is small, it can reduce generating of the fault in the process of manufacturing a label, a bag, etc. from this film roll. Even if it is a case where high contraction is required selectively, beautiful contraction result appearance can be comparatively acquired by contraction in a low temperature region. Such a film roll can be obtained with the manufacturing method of this invention. Therefore, the heat contraction nature polyester system film roll of this invention is preferred as a film roll for manufacturing the various covering labels etc. which make full labels, such as a PET bottle, the start.

[Best Mode of Carrying Out the Invention]

[0016]

As a result of examining various faults which occur at the process of manufacturing a label, a bag, etc. from a heat contraction nature polyester system film roll, and a heat contraction process, this invention persons these defects. It found out that it was easy to generate in the case of polyester containing a component unit secondary in addition to the main component unit from which raw material polyester of a film is obtained not with gay polyester but with copolymerization and a blend. That is, the composition change of polyester occurred in the long film, and it was thought that this was one factor of change of a heat contraction action. And when it was a heat contraction nature polyester system film roll concerning this invention, since change

of a composition change or a heat contraction action was small, it found out not causing the above-mentioned fault.

[0017]

At the process which carries out covering contraction to a container etc., the label made from a heat contraction nature film usually. In an above-mentioned hot wind tunnel, the inside of the hot wind of about 120–200 \*\* and about 2–20 m/second of wind speeds is passed in about 2 to 20 seconds, and it carries out by passing the inside of about 75–95 \*\* and the steam of about 0.5–20 MPa of pressures in about 2 to 20 seconds in a steam tunnel. As opposed to containers, such as a PET bottle which has complicated side shape in this invention, for example, Even if it uses it as a heat contraction nature label for containers which has the side shape which uses this the greater part of side as a heat contraction nature label of a wrap sake, or requires partial very high contraction of a wrap label for the side (even if it uses it for for example, the full label for PET bottles, the full label for glass bottles, etc.), The heat contraction characteristic required for a film was specified so that very beautiful contraction result appearance could be attained. Hereafter, this invention is explained in detail.

[0018]

The heat contraction nature film roll of a polyester system is the target of this invention. In the broad temperature region from low temperature to an elevated temperature, it has the outstanding contraction result nature, and contraction spots, wrinkles, and little contraction finishing appearance can be acquired, and a beautiful glossy sense and transparency can be acquired.

[0019]

The heat contraction nature polyester system film currently wound around the heat contraction nature polyester system film roll of this invention must satisfy requirement (A) – (C). When requirements (A) roll the end by the side of the cut water of the film in the constant region whose film properties are stable in the length direction of the film currently wound around the roll the 1st end and the end by the side of the end is used as the 2nd end, From the 2nd end of the above, provide the last logging part in less than 2 m of the inside from the 1st end of the above again at less than 2 m of the inside, and the 1st sample logging part. A sample logging part is provided every about 100 m from the 1st sample logging part, The average value of the heat shrinkage rate of a maximum shrinkage direction when the sample started 10 cm x 10 cm in the shape of a square, respectively was immersed for 5 seconds into 70 \*\* warm water, and was raised, and it is immersed for 10 seconds subsequently to

underwater [ 25 \*\* ] and pulls up is 10 to 50%.

[0020]

First, the meaning of "the constant region whose film properties are stable in the length direction of a film" of the above-mentioned requirements (A) is explained. "The constant region whose film properties are stable in the length direction of a film" is a field where it is carried out by stabilizing a film production process and a stretching process at the time of film manufacture, and film properties show a uniform state mostly. In this invention, it is making to equalize conventionally more highly than a level the amount of most secondary component units, and the other characteristics into technical idea in the long film obtained when operated by the stationary state where the film production process and the stretching process were stabilized. A real operation top does not require equalization even of the film obtained when the amount of feeding and film production conditions were unstable in this invention, although the presentation of a film may be changed by the feeding method or film production conditions during film manufacture. For this reason, it made into the precondition to perform a sampling only in the field currently operated by the stationary state where the film production process and the stretching process were stabilized, i.e., a "constant region", when evaluating the characteristic of requiring equalization.

[0021]

Therefore, for example, if it is a film when about 10m is not operated steadily from the cut water of the roll, it will not sample from this portion but the 10th m will be sampled as the 1st end of a film from a cut water.

[0022]

The number of said constant regions (steady operation field) is usually one (the whole film roll is covered and it is one place) per film roll. However, since it may be also when it exists in two or more places depending on a manufacturing situation, it samples only from a constant region in this case. Said constant region can be evaluated by, for example, measuring the heat shrinkage rate of the maximum shrinkage direction of the film at 85 \*\* by the method of mentioning later. Namely, what is necessary is just to regard the place where the heat shrinkage rate serves as less than about 20% of width (the difference of the maximum of the heat shrinkage rate of two or more samples and the minimum is less than about 20%) as it being a constant region.

[0023]

Then, the method of a sampling is explained. When the end by the side of the cut water of the film in the above-mentioned constant region is rolled the 1st end and the end by the side of the end is used as the 2nd end about the film currently wound

around the roll of one, From the 2nd end of the above, provide the last logging part in less than 2 m of the inside from the 1st end of the above again at less than 2 m of the inside, and the 1st sample logging part. By providing a sample logging part every about 100 m from the 1st sample logging part, the overall length of the constant region of a film is covered and a sample is chosen as abbreviation regular intervals. "Every about 100 m" means [ about /  $100m \times 1m$  ] that a sample may be started by the way.

[0024]

The above-mentioned sampling is explained more to details. For example, when the 498-m-long heat contraction nature film [ an overall length / in a constant region ] is wound around the roll, sample No.1 of the beginning is cut off from a film finishing (the 2nd end) winding before less than 2 m. The area to cut off is suitably set up according to the property value to measure. Then, 2nd sample No.2 is cut off in the place about 100 m away from the place which cut off sample No.1 of the beginning. Similarly, by the 200th [ about ] m, 4th sample No.4 is cut off by the 300th [ about ] m, and 5th sample No.5 is cut off for 3rd sample No.3 by the 400th [ about ] m. Here, since the remainder becomes shorter than 100 m, 6th sample (last) No.6 cuts out less than 2-m one of portions from the cut water (the 1st end) of a film.

[0025]

All the samples of the shape of a square (10 cm x 10 cm) which carried out said requirements for this invention (A) in this way, and was cut off, The average value of the heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 70 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up is 10 to 50%. With such a film, the heat contraction nature label which serves as high contraction by short-time processing comparatively can be provided.

[0026]

When the heat shrinkage rate measured on condition of (A) is less than a mentioned range, low-temperature shrinkage characteristics will need to become insufficient, and it will be necessary to make high temperature at the time of label covering contraction, and is not desirable. On the other hand, when the heat shrinkage rate measured on condition of (A) exceeds a mentioned range, it is in the tendency which defects, such as a jump (shift up when a film contracts rapidly) of the label by heat contraction, produce. As for the heat shrinkage rate measured on condition of (A), it is more preferred that it is [ not less than 15% ] 40% or less.

[0027]

Here, the heat shrinkage rate of a maximum shrinkage direction means the heat

shrinkage rate in the direction which the sample contracted most, and a maximum shrinkage direction is decided by the cut-off length of the lengthwise direction of a square sample, or a transverse direction. A heat shrinkage rate (%) a sample (10 cm x 10 cm) in warm water with a regular measurement temperature of \*\*0.5 \*\*, After being immersed for 10 seconds, carrying out heat contraction by no load condition and being immersed in 25 \*\* underwater [ \*\*0.5 \*\* ] for 10 seconds by no load condition, It is the value which measured the length of a film, and the lateral length and was calculated according to the following formula (the heat shrinkage rate of the maximum shrinkage direction measured on this condition is only hereafter abbreviated to a "heat shrinkage rate").

[0028]

Heat shrinkage rate = $100 \times (\text{length after the length-contraction before contraction}) / (\text{length before contraction})$

Next, requirements (B) about each sample of the shape of a square (10 cm x 10 cm) separately started from each sample logging part in requirements (A). The average value of the heat shrinkage rate of a maximum shrinkage direction when it was immersed for 5 seconds into 85 \*\* warm water, and it pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up is not less than 75%, and said heat shrinkage rate of all the samples is settled in less than \*\*5% of range of said average heat shrinkage rate.

[0029]

When the average value of the heat shrinkage rate of the maximum shrinkage direction measured on condition of (B) is smaller than 75%, when a PET bottle etc. are made to carry out covering contraction as a label, it is in the tendency which the shortage of contraction produces in the portions (for example, opening part of a bottle, etc.) as which bigger contraction is required, for example. It is not less than 78% more preferably. As for the average value of the heat shrinkage rate of the maximum shrinkage direction measured on condition of (B), it is preferred that it is 95% or less.

[0030]

In the requirements for (B), the heat shrinkage rate of all the samples is required also for having fitted in less than \*\*5% of range of an average heat shrinkage rate. Measure the heat shrinkage rate of a maximum shrinkage direction on the above conditions (B) about all the started samples, and the average value by X (%). When content is set to Y1 (%) for the heat shrinkage rate of sample No.1,  $|X-Y1|$  (absolute value of X-Y1) is smaller than 5 (%), In the heat shrinkage rate (%) about sample No.2-No.6, that each  $|X-Yn|$  is smaller than 5 (%) means less than \*\*5% of an average heat shrinkage rate

similarly, if it puts in another way -- both a difference with the maximums  $Y_{max}$  and  $X$  of  $Y_n$ , and a difference with the minimums  $Y_{min}$  and  $X$  -- although -- if it is less than \*\*5%, the above-mentioned requirements will be satisfied.

[0031]

Since change of heat contraction actions, such as one piece, one label, and a bag, becomes small, the defect in the process which carries out covering contraction can decrease, and the defective fraction of a product can be made to decrease sharply by making small change of the heat shrinkage rate of the heat contraction nature film currently wound around the roll of one. As for the change degree of the heat shrinkage rate in requirements (B), it is more preferred that it is less than \*\*3% of average value, and less than \*\*2% of its average value is still more preferred. Also in the heat shrinkage rate measured on the above mentioned requirements for (A), it is preferred that a change degree is \*\*5% of average value.

[0032]

As for the average value of the heat shrinkage rate (direction-crossing-at-a-right-angle heat shrinkage rate) of the direction which intersects perpendicularly with the maximum shrinkage direction measured on condition of (B), it is preferred that it is 10% or less. When exceeding 10%, it becomes easy to generate the appearance defect by TATEHIKE. "TATEHIKE" is that the length of the label after contraction becomes irregular, and the appearance defect which draws the line where the upper bed edge of the label after making a PET bottle etc. carry out covering contraction curves downward, or draws the line where a lower end edge curves upward is said. As for the average value of the direction-crossing-at-a-right-angle heat shrinkage rate measured on condition of (B), it is more preferred that it is 7% or less. It is desirable for the measured value of not only average value but all the samples to be 10% or less (preferably 7% or less).

[0033]

In addition, the film currently wound around the heat contraction nature polyester system film roll of this invention needs to satisfy requirements (C). Each sample of the shape of a square (10 cm x 10 cm) separately started from each sample logging part [ in / in requirements (C) / requirements (A) ], About each sample cut off 10 cm x 10 cm in the shape of a square after making a maximum shrinkage direction carry out heat contraction of the piece of logging of the shape of a square (25 cm x 25 cm) separately started from each sample logging part in requirements (A) 10%. When making into  $X_0$  (%) and  $X_{10}$  (%) the heat shrinkage rate of the maximum shrinkage direction measured when it was immersed for 5 seconds into 95 \*\* warm water, and it

pulled up, and it is immersed for 10 seconds subsequently to underwater [ 25 \*\* ] and pulls up, respectively, The heat shrinkage rate difference delta (%) shown by the lower formula in all the sample logging parts is settled in 10 to 20% of range,

$$\text{delta} = X_0 - X_{10}$$

It says. The sample for measuring  $X_0$  and the sample for measuring  $X_{10}$  should be started from the same sample logging part. The above-mentioned heat shrinkage rate  $X_{10}$  is measured as follows. First, the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is produced. The mold which counters and has two zippers is prepared so that only the end of the lot which a rectangular film counters can be grasped. A heat contraction nature polyester system film is judged in a square or a rectangle in parallel with a maximum shrinkage direction. The film after decision is fixed with a described [ above ] type. Immobilization is performed by slackening a film so that the both ends which intersect perpendicularly with the maximum shrinkage direction of this film may be grasped by a zipper and the film length between zippers and the ratio of the distance between zippers of a mold may be set to 1:0.9. Then, after immersing the film fixed to the mold for 5 seconds and carrying out heat contraction by no load condition into 95 \*\* \*\*0.5 \*\* warm water, promptly, by no load condition, it is immersed for 10 seconds in 25 \*\* underwater [ \*\*0.5 \*\* ], and pulls up to it. This film is removed from a mold, attached groundwater is removed, and the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is obtained.

[0034]

A sample (10 cm x 10 cm) is judged from the obtained film, heat shrinkage rate  $X_{10}$  is measured using this sample by the same method as the above-mentioned heat shrinkage rate  $X_0$ , and the heat shrinkage rate difference delta is computed by an upper type (1). As for each of time until it goes into a sample cutting process from the making process of the film made [ the maximum shrinkage direction ] to carry out heat contraction 10%, and time until it goes into the heat contraction process in the conditions of (C) from a sample cutting process, it is desirable to consider it as a short time as much as possible. When keeping the sample judged when the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% was kept to a sample cutting process to a heat contraction process, it is in an atony state, and it places in the air and under the environment of 25 \*\* or less, and unnecessary heat contraction is kept from arising.

[0035]

If the above-mentioned heat shrinkage rate difference delta is a film which becomes in

a mentioned range, the heat contraction nature label which has a reinforcing effect of a covering container can be obtained. When the above-mentioned heat shrinkage rate difference delta is less than a mentioned range, the reinforcing effect of the container after covering contraction when it uses for a label use becomes insufficient. The more desirable heat shrinkage rate difference delta is 17% or less. Since the above-mentioned heat shrinkage rate  $X_{10}$  is a value measured using the film which carried out heat contraction 10%, the minimum of the heat shrinkage rate difference delta is not less than 10%.

[0036]

Incidentally with the usual heat contraction nature polyester system film. Once carrying out heat contraction 10%, the final heat shrinkage rate (sum total of 10% of the first heat shrinkage rate, and the 2nd heat shrinkage rate) at the time of carrying out heat contraction again, It falls more greatly than the heat shrinkage rate in the case of having shrunk the film before heat contraction thoroughly on the same heat contraction conditions (that is, the above-mentioned heat shrinkage rate difference delta will exceed a mentioned range). In the film roll of this invention, the presentation of the polyester used for a film is made suitable so that it may mention later, and it is supposed that the extension conditions of a film are controlled and the heat shrinkage rate difference delta in a mentioned range will be secured. It is preferred that the change degree of delta is also small, and when the average value of delta is computed, delta of all the samples has less than \*\*3% of the preferred average value of delta.

[0037]

About the sample started in the film roll of this invention from each sample logging part which the requirements for the above (A) explained by the way. When the thermal-shrinkage-stress value about this direction of the film after carrying out heat contraction to a maximum shrinkage direction 10% is measured on with specimen 20 mm in width, and a distance between zippers of 100 mm conditions among a 5 m [ in the temperature of 90 \*\*, and blow-off speed ]/second hot wind, It is preferred that the average value of the maximum-heat-shrinkage-stress value of each sample is 7 or more MPa. If the average value of the above-mentioned maximum-heat-shrinkage-stress value is a film of 7 or more MPa, the heat contraction nature label in which the reinforcing effect of the covering container was more excellent can be obtained. That is, the average value of the above-mentioned maximum-heat-shrinkage-stress value is in the tendency for the effect of reinforcing a covering container to fall, in the heat contraction nature label obtained from the film which is less than a mentioned range. As for the average value of the

above-mentioned maximum-heat-shrinkage-stress value, it is more preferred that they are 10 or more MPa, and it is still more preferred that they are 11 or more MPa.

[0038]

The above-mentioned maximum-heat-shrinkage-stress value is measured by the following methods.

[1] From said each sample logging part, the length of a maximum shrinkage direction cuts down the specimen which are 200 mm and 20 mm in width.

[2] Heat the inside of the heating furnace of the tension tester (for example, product made from an Oriental energy machine "tensilon") provided with the hot wind type heating furnace at 90 \*\*.

[3] Stop air blasting and set a specimen in a heating furnace. The distance between zippers shall be 100 mm (fixed), and the length between zippers of a specimen and the distance between zippers slack a specimen, and set it so that it may be set to 1:0.9.

[4] Shut the door of a heating furnace promptly and resume air blasting (5 m [ in the temperature of 90 \*\*, and blow-off speed ]/second hot wind). Heat contraction of the specimen is carried out 10%, and the thermal shrinkage stress after this heat contraction is detected and measured.

[5] The maximum is read in a chart and let this be a maximum-heat-shrinkage-stress value (MPa).

[0039]

In the long film currently wound around the roll, it is preferred that thickness is uniform because of the poor occurrence prevention for every label. Therefore, when thickness displacement measurement in the maximum shrinkage direction of the film in each sample logging part is performed about a specimen 50 cm in length, and 5 cm in width, the thickness distribution specified at a lower ceremony (2) is measured about all the samples and the average is taken, it is recommended that the average value of thickness distribution is 6% or less.

Thickness distribution = [(the maximum thickness-minimum thickness) /average thickness] x100 (2)

The above-mentioned thickness distribution is 50 cm in length, and 5 cm in width in each sample logging part, Create ten specimens which make the maximum shrinkage direction of a film the length direction, and about each specimen. Contact process thickness meters, such as for example, "KG60/A" (by ANRITSU CORP. etc.), are used, After measuring the thickness of the length direction continuously, outputting to a chart, asking for maximum thickness, the minimum thickness, and average thickness from this output and computing thickness distribution using an upper type (2) from

these, it is obtained by calculating the average value of the thickness distribution of ten specimens.

[0040]

In a film with the average value of greater than 6% of the above-mentioned thickness distribution, it is presswork, the printability at the time of printing a multicolor pattern especially is inferior, and when piling up two or more colors, it is easy to produce gap. In order to manufacture a label from the film of this invention, when carrying out solvent bonding and tube--ization-processing it, superposition of the adhesion part of a film becomes difficult. When the average value of the above-mentioned thickness distribution rolls round to rolled form in the film exceeding 6%, the difference of partial volume hardness arises and the slack and wrinkles of a film resulting from this occur, and also when it becomes impossible to use it as a heat contraction nature film, it is. 3% or less of the average value of the above-mentioned thickness distribution is still more desirable, and is desirable. [ especially 2% or less of ]

[0041]

It is preferred that the melt resistivity value in 275 \*\* of a film is below  $0.70 \times 10^8$  omega-cm in this invention. Thus, if a melt resistivity value is small, it faces cooling the film which carried out melting extrusion from the extrusion machine with a casting roll, and the electrostatic adhesion of the film to a roll can be improved. Therefore, the stability of cooling solidification can be improved and casting speed (production rate) can be raised. As for a melt resistivity value, it is more preferred that it is below  $0.65 \times 10^8$  omega-cm, and it is still more preferred that it is below  $0.60 \times 10^8$  omega-cm. Let the above-mentioned melt resistivity value be the average value of the sample started from each sample logging part.

[0042]

Film quality can also be raised, if a melt resistivity value is low and electrostatic adhesion is high. Namely, when electrostatic adhesion is low, the cooling solidification of a film becomes imperfect, exhaust air enters locally between a casting roll and a film, and there is a possibility that a pinner bubble (stripe-like defect) may occur in a film surface, but. If excelled in electrostatic adhesion, generating of said pinner bubble can be reduced and film appearance can be made good.

[0043]

In addition, the thickness of a film can be equalized, when a melt resistivity value is low enough and electrostatic adhesion is high enough. Namely, if the electrostatic adhesion to a casting roll is low, the thickness of the cast unstretched film original fabric will become uneven, and the heterogeneity of thickness will be expanded more

in the oriented film which extended this unstretched film, but. When electrostatic adhesion is high enough, thickness can be equalized also in an oriented film.

[0044]

In order to control the melt resistivity value of a film to a mentioned range, it is desirable to make an alkaline earth metal compound and the Lynn content compound contain in a film. Although at least an alkaline earth metal compound can lower a melt resistivity value, if the Lynn content compound is made to live together, a melt resistivity value can be lowered remarkably. Although the Reason for the ability to reduce a melt resistivity value remarkably by combining an alkaline earth metal compound and the Lynn content compound is not clear, by making the Lynn content compound contain, the quantity of a foreign matter can be decreased and it is presumed because the quantity of a charge carrier can be increased.

[0045]

As for the content of the alkaline earth metal compound in a film, it is preferred to use more than 40 ppm (it is [ a mass basis and the following ] the same) on the basis of alkaline-earth-metals atom  $M^2$ , for example, it is more preferred to be referred to as not less than 50 ppm, and it is still more preferred to be referred to as not less than 60 ppm. When there is too little quantity of an alkaline earth metal compound, it is to lower a melt resistivity value in the tendency which becomes difficult. Even if it increases content of an alkaline earth metal compound too much, the reduction effect of a melt resistivity value is saturated and it is in the tendency for evils, such as foreign matter generation and coloring, to become large rather. Therefore, as for the content of an alkaline earth metal compound, it is preferred to be referred to as 400 ppm or less on the basis of alkaline-earth-metals atom  $M^2$ , for example, it is more preferred to be referred to as 350 ppm or less, and it is still more preferred to be referred to as 300 ppm or less.

[0046]

As for the content of the Lynn content compound in a film, it is preferred to use more than 10 ppm (it is [ a mass basis and the following ] the same) on the basis of phosphorus atom P, for example, it is more preferred to be referred to as not less than 15 ppm, and it is still more preferred to be referred to as not less than 20 ppm. If there is too little quantity of the Lynn content compound, it may become difficult to fully lower a melt resistivity value, and the generated amount of a foreign matter cannot be reduced. Even if it increases content of the Lynn content compound too much, the reduction effect of a melt resistivity value will be saturated. Furthermore generation of a diethylene glycol is promoted, and since it is difficult to control the generated

amount moreover, there is a possibility of differing from what film properties were planning. Therefore, as for the content of the Lynn content compound, it is preferred to be referred to as 500 ppm or less on the basis of phosphorus atom P, for example, it is more preferred to be referred to as 450 ppm or less, and it is still more preferred to be referred to as 400 ppm or less.

[0047]

As for the mass ratio ( $M^2/P$ ) of alkaline-earth-metals atom  $M^2$  in a film, and phosphorus atom P, when lowering the melt resistivity value of a film with an alkaline earth metal compound and the Lynn content compound, it is desirable that it is 1.5 (1.7 or more [ 1.6 or more / Preferably / still more preferably ]) or more. By making a mass ratio ( $M^2/P$ ) or more into 1.5, a melt resistivity value can be reduced remarkably. If a mass ratio ( $M^2/P$ ) exceeds 5.0, the generated amount of a foreign matter may increase, or the generated amount of a foreign matter may increase, or a film may color. Therefore, as for a mass ratio ( $M^2/P$ ), it is preferred to use 5.0 or less, it is more preferred to use 4.5 or less, and it is still more preferred to use 4.0 or less.

[0048]

In order to lower the melt resistivity value of a film further, it is desirable to make an alkali metal compound contain in a film in addition to the above-mentioned alkaline earth metal compound and the Lynn content compound. Even if it makes a film contain an alkali metal compound independently, it cannot lower a melt resistivity value, but it can lower a melt resistivity value remarkably by adding to the coexistence system of an alkaline earth metal compound and the Lynn content compound. Although it is not clear about the Reason, it is presumed by forming a complex by three persons of an alkali metal compound, an alkaline earth metal compound, and the Lynn content compound that the melt resistivity value is lowered.

[0049]

The content of the alkali metal compound in a film, It is preferred to use more than 0 ppm (it is [ a mass basis and the following ] the same) on the basis of alkaline metal atom  $M^1$ , it is more preferred to be referred to as not less than 5 ppm, it is still more preferred to be referred to as not less than 6 ppm, and especially the thing set to not less than 7 ppm is preferred. Even if it increases content of an alkali metal compound too much, the reduction effect of a melt resistivity value is saturated and the generated amount of a foreign matter increases further. Therefore, as for the content of an alkali metal compound, it is preferred to be referred to as 100 ppm or less on the basis of alkaline metal atom  $M^1$ , it is more preferred to be referred to as 90 ppm or less, and it is still more preferred to be referred to as 80 ppm or less.

[0050]

As the above-mentioned alkaline earth metal compound, hydroxide of alkaline-earth metals, an alkoxide, an aliphatic-carboxylic-acid salt (preferably acetate, such as acetate and butyrate), an aromatic-carboxylic-acid salt (benzoate), salts (salt with phenol, etc.) with the compound which has a phenolic hydroxyl group, etc. are mentioned. As alkaline-earth metals, magnesium, calcium, strontium, barium (preferably magnesium), etc. are mentioned. Magnesium acetate is contained especially in a desirable alkaline earth metal compound magnesium hydroxide, magnesium methoxide, magnesium acetate, calcium acetate, strontium acetate, barium acetate, etc. The above-mentioned alkaline earth metal compound is independent, or it can be used, combining it two or more sorts.

[0051]

As the above-mentioned Lynn content compound phosphoric acid (phosphoric acid, phosphorous acid, hypophosphorous acid, etc.). And the ester (alkyl ester, aryl ester, etc.) and alkyl phosphonic acid, aryl phosphonic acid, and those ester (alkyl ester, aryl ester, etc.) are mentioned. As desirable phosphorus compounds, it is aliphatic series ester (alkyl ester of phosphoric acid, etc.; for example) of phosphoric acid and phosphoric acid. Phosphoric acid mono-  $C_{1-6}$  alkyl ester, such as phosphoric acid monomethyl ester, phosphoric acid monoethyl ester, and phosphoric acid monobutyl ester, \*\*\*\*\*  $C_{1-6}$  alkyl ester, such as phosphodimethyl ester, phosphodi-ethyl ester, and dibutyl phosphate ester, Phosphoric acid Tori  $C_{1-6}$  alkyl ester, such as trimethyl phosphate ester, phosphoric acid triethyl ester, and tributyl phosphate ester etc., Aromatic ester (mono- \*\* JI or Tori  $C_{6-9}$  aryl ester of phosphoric acid, such as triphenyl phosphate and tricresyl phosphate, etc.) of phosphoric acid, aliphatic series ester of phosphorous acid (alkyl ester of phosphorous acid, etc.; for example) Mono- \*\* JI of phosphorous acid, such as phosphorous acid trimethyl \*\* phosphorous acid tributyl, or alkyl phosphonic acid ( $C_{1-6}$  alkyl phosphonic acid, such as methylphosphonic acid and ethylphosphonic acid) and alkyl phosphonic acid alkyl ester (dimethyl methylphosphonate.), such as Tori  $C_{1-6}$  alkyl ester Mono- \*\*\*\* of  $C_{1-6}$  alkyl phosphonic acid, such as ethyl dimethyl phosphonate, JI  $C_{1-6}$  alkyl ester etc., aryl phosphonic acid alkyl ester (dimethyl phenylphosphonate.) Mono- \*\*\*\* of  $C_{6-9}$  aryl phosphonic acid, such as diethyl phenylphosphonate, JI  $C_{1-6}$  alkyl ester etc., Aryl phosphonic acid aryl ester (mono- \*\*\*\* of  $C_{6-9}$  aryl phosphonic acid, such as diphenyl phenylphosphonate, is JI  $C_{6-9}$  aryl ester etc.) etc. can be illustrated. Phosphoric acid and phosphoric acid trialkyl (trimethyl phosphate etc.) are especially contained in the desirable Lynn content compound. These Lynn content compound is independent, or

it can be used, combining it two or more sorts.

[0052]

As the above-mentioned alkali metal compound, hydroxide of an alkaline metal, carbonate, an aliphatic-carboxylic-acid salt (preferably acetate, such as acetate and butyrate), an aromatic-carboxylic-acid salt (benzoate), salts (salt with phenol, etc.) with the compound which has a phenolic hydroxyl group, etc. are mentioned. Lithium, sodium, potassium (preferably sodium), etc. are mentioned as an alkaline metal.

Sodium acetate is contained especially in a desirable alkaline earth metal compound lithium hydroxide, sodium hydroxide, a potassium hydrate, lithium carbonate, sodium carbonate, potassium carbonate, lithium acetate, sodium acetate, potassium acetate, etc.

[0053]

The film in the heat contraction nature polyester system film roll of this invention has an ester unit formed from a polyvalent carboxylic acid component and a polyhydric alcohol component as a main component unit.

[0054]

As polyvalent carboxylic acid for forming a polyvalent carboxylic acid component in an ester unit, Aliphatic dicarboxylic acid, such as aromatic-dicarboxylic-acid; adipic acid, such as terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and alt.phthalic acid, azelaic acid, sebacic acid, and decane dicarboxylic acid; these ester formation derivatives, such as alicyclic dicarboxylic acid;, are mentioned.

[0055]

When using above-mentioned aliphatic dicarboxylic acid, it is preferred that polyvalent carboxylic acid component 100 mol % Naka of a film and an aliphatic dicarboxylic acid component are less than [ 3 mol % ]. Although mentioned later for details, in order to demonstrate tear-proof nature, intensity, heat resistance, etc. in the heat contraction nature polyester system film of this invention, it is desirable to use an ethylene terephthalate unit as a main component unit. Therefore, although it is recommended that a terephthalic acid component serves as a subject, the polyvalent carboxylic acid component in a film, When the amount of aliphatic dicarboxylic acid components is more than 3 mol %, in the heat contraction nature label obtained from this film, only the rigidity (waist of a film) which can be equal to high-speed wearing in a container may not be obtained.

[0056]

As for the polyvalent carboxylic acid (for example, trimellitic acid, pyromellitic acid, these anhydrides, etc.) more than trivalent, not using is preferred. In the heat

contraction nature polyester system film which has these polyvalent carboxylic acid components, sufficient heat shrinkage rate may become is hard to be acquired.

[0057]

As a polyhydric alcohol class for forming a polyhydric alcohol component in an ester unit, in order to form an ethylene terephthalate unit, ethylene glycol is used. In addition, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, Aliphatic series diol, such as 2-methyl-1,5-pentanediol and 2,2-diethyl-1,3-propanediol, Alicyclic diol, such as 1,4-cyclohexane dimethanol, dimer diol, a bisphenol compound, or the alkylene oxide adduct of the derivative can be used together.

[0058]

the film of this invention -- diol (for example, propylene glycol.) of the carbon numbers 3-6 It is preferred to use one or more sorts and the polyester which adjusted glass transition temperature (Tg) to 60-75 \*\* using 1,4-cyclohexane dimethanol among 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, etc.

[0059]

It is desirable to use especially the polyester which used neopentyl glycol together in respect of reservation of each of above-mentioned heat shrinkage rates, the improvement in contraction result appearance, and container reinforcing effect reservation. polyhydric alcohol component % of 100 mol of a film -- inside and a neopentyl glycol component amount -- more than 15 mol % -- it is more than 18 mol % preferably, and it is recommended less than 27 mol % and that it is less than 25 mol % preferably. moreover -- the case where diol of carbon numbers 3-6 other than neopentyl glycol is used -- polyhydric alcohol component % of 100 mol of a film -- inside and these diol components -- more than 3 mol % -- it is more than 5 mol % preferably, and it is desirable less than 15 mol % and that it is less than 13 mol % preferably. In addition, in the case where 1 and 4-cyclohexane dimethanol is used. polyhydric alcohol component % of 100 mol of a film -- inside and 1 and 4-cyclohexane dimethanol component amount -- more than 15 mol % -- it is more than 18 mol % preferably, and less than 27 mol % and using less than 25 mol % preferably are recommended.

[0060]

As for diol (for example, octanediol etc.) of eight or more carbon numbers except the suitable polyhydric alcohol class of the above-mentioned illustration, and polyhydric alcohol more than trivalent, not using is preferred. In the heat contraction nature polyester system film which has these diol components and polyhydric alcohol

components, sufficient heat shrinkage rate may become is hard to be acquired.

[0061]

Although it is not a polyhydric alcohol class, a part of lactone represented by epsilon-caprolactone may be used. Lactone serves as a unit which carries out ring breakage and has an ester bond to both ends.

[0062]

If the tear-proof nature of a film, intensity, heat resistance, etc. are taken into consideration, it is preferred to choose so that component unit 100 mol % Naka of a heat contraction nature polyester system film and an ethylene terephthalate unit may become more than 50 mol %. Therefore, it is preferred to make more than 50 mol %, polyhydric alcohol component 100 mol % Naka, and an ethylene glycol component more than 50 mol % for polyvalent carboxylic acid component 100 mol % Naka and a terephthalic acid component (ingredient which consists of terephthalic acid or its ester). More than 55 mol % of an ethylene terephthalate unit is more preferred, and more than its 60 mol % is still more preferred.

[0063]

Although the polyester which constitutes a heat contraction nature polyester system film can be manufactured by carrying out melt polymerization with a conventional method, . Carry out the polycondensation of the oligomer by which the direct reaction of polyvalent carboxylic acid and the polyhydric alcohol class might be carried out. After carrying out the ester exchange reaction of what is called a direct polymerization method, and the methyl ester object and polyhydric alcohol of polyvalent carboxylic acid, what is called an ester interchange method etc. that carry out a polycondensation are mentioned, and arbitrary manufacturing methods can be applied. It may be polyester obtained by other polymerization methods. The degree of polymerization of polyester is made into intrinsic viscosity, and is preferred. [ of the thing of 0.3 – 1.3 dl/g ]

[0064]

As a polymerization catalyst, can use conventional various catalysts, and For example, a titanium system catalyst, An antimony system catalyst, a germanium system catalyst, a tin series catalyst, a cobalt system catalyst, Titanium system catalysts (titanium tetrabutoxide etc.), antimony system catalysts (antimonous oxide etc.), a germanium system catalyst, cobalt (diacid-ized germanium etc.) system catalysts (cobaltous acetate etc.), etc. are mentioned preferably a manganese system catalyst etc.

[0065]

The addition stage in particular of an alkali metal compound, an alkaline earth metal compound, and the Lynn content compound is not limited, Before an esterification reaction and during esterification, although it may be which stage from the end of esterification before a polymerization process start, under polymerization, and after a polymerization, it is from the end of esterification before a polymerization process start preferably to the desirable arbitrary stages after an esterification process, and a pan. If an alkaline earth metal compound and the Lynn content compound (and accepting necessity alkali metal compound) are added after an esterification process, the generated amount of a foreign matter can be reduced compared with the case where it adds before it.

[0066]

If needed, particles, such as silica, a titanium dioxide, kaolin, and calcium carbonate, may be added to a film material, and an antioxidant, an ultraviolet ray absorbent, a spray for preventing static electricity, colorant, an antimicrobial agent, etc. can also be added further.

[0067]

Next, the desirable manufacturing method of the long film in which an overall length is covered and a uniform presentation and a heat contraction action are shown is explained.

[0068]

Generally a heat contraction nature polyester system film, From a viewpoint of reconciling the heat contraction characteristic, intensity, etc., blend the polyester in which a kind differs from two or more sorts of presentations, or a copolymerization monomer component is made into plurality, The technique to which the characteristic of the film produced by introducing a secondary component unit into raw material polyester in addition to a main component unit is changed is adopted. At this time, there are a method which performs copolymerization and carries out single use of this copolymerized polyester as a means to make one or more secondary component units contain in a film, and a method which blends different gay polyester or copolymerized polyester of a kind. Although change of a film presentation hardly takes place in the long film wound around the roll, a heat contraction action may differ in the method which carries out single use of the copolymerized polyester by extension conditions.

[0069]

On the other hand, in the blend method, since the characteristic of a film can be easily changed only by changing a blend ratio and it can respond also to the industrial production of the film of a various kind, it is carried out widely industrially. It is

preferred to specifically blend and use two or more sorts of polyester in which  $T_g(s)$  differ in the blending method. The polyester to blend may be three or more sorts. By blending and using two or more sorts of polyester, polyester does not dissolve but we are anxious about the trouble of a film milking, for example. However, the ester exchange reaction arose by being heated in the film extrusion process mentioned later, and as a result of the whole polyester contained in a film turning into copolymerized polyester, it has usually become clear that troubles, such as the above-mentioned white blush mark, are avoided.  $T_g$  measured by the publicly known method about the film obtained from two or more sorts of polyester blends in which  $T_g(s)$  differ, for example can check copolymer-ization by such an ester exchange reaction from becoming a single value.

[0070]

However, especially in the above polyester blends, since it is found out that the composition change and physical-properties change of the film wound around the roll of one become large, in order to obtain the film roll with which it is satisfied of the requirements specified by this invention, it is preferred to use the following technique.

[0071]

(1) Equalization of chip shape

In a blend method, after usually blending within a hopper several raw material polyester chips from which a presentation differs, a chip mixture is introduced into an extrusion machine, and melt kneading of the polyester is carried out, it is extruded, and is film-ized. When there is three kinds of polyester used as a raw material, supply each polyester chip to continuous system or an intermittent type at three hoppers, and for example, via a buffer hopper if needed, Eventually, mixing three kinds of polyester chips just before an extrusion machine or with a hopper (it is called the "last hopper" for convenience) right above, according to the extrusion outlet of an extrusion machine, a raw material chip is quantitatively supplied to an extrusion machine, and a film is formed. However, when the case where there are many amounts of chips in the last hopper, and a residue decreased depending on the capacity or shape of the last hopper, it was found out by this invention person etc. that the phenomenon of the raw material segregation that the presentations of the chip supplied to an extrusion machine from the last hopper differ has occurred. This problem appears notably especially, when the shape or the specific gravity of various polyester chips is different. As a result, the polyester presentation of a long film will be changed.

[0072]

Therefore, when most polyester of the amount used and this polyester manufacture a heat contraction nature polyester system film roll including the process of mixing and carrying out melting extrusion of one or more sorts of other polyester in which presentations differ, In order to obtain a film with little change of film properties with which it is satisfied of said each requirement, it is preferred to double the shape of two or more sorts of polyester chips to be used as a means to reduce the composition change of the polyester which constitutes a film, and to deter the raw material segregation within the last hopper.

[0073]

In order to manufacture the raw material chip of polyester film, after picking out polyester of a molten state from a polymerization apparatus by strand shape and usually water-cooling it promptly after a polymerization, the method of cutting with a strand cutter is adopted. For this reason, the chip of polyester usually serves as an elliptic cylindrical shape of an ellipse form [ section ]. At this time, as a raw material chip of other polyester mixed by most polyester chips of the amount used, When using what is less than \*\*20% of range, respectively to the diameter of average length (mm), the average minor axis (mm), and average chip length (mm) of most polyester of a section ellipse, it traced that the above-mentioned raw material segregation might be reduced. [ of the amount used ] [ of a raw material chip ] It is more preferred that these average value uses the thing of less than \*\*15% of range, respectively.

[0074]

If a chip size has a difference, when the mixture of the chip falls the inside of the last hopper, since a small chip falls easily previously, if its chip residue in the last hopper decreases, the ratio of a large chip will increase and this will cause a raw material segregation. However, by using the chip in a mentioned range, these raw material segregations can be reduced and a long film with a uniform film presentation can be obtained.

[0075]

(2) Rationalization of hopper shape

In obtaining a film, an extrusion machine is used, but rationalization of the last hopper shape is also a desirable means for obtaining a long film with a uniform presentation. That is, it is because only a small chip will fall previously and will cause a raw material segregation, if the angle of inclination of a funnel-like hopper is smaller than 65 degrees. It can be made easy to drop on an angle of inclination using a not less than 65-degree hopper like a chip also with a small large chip, and in order to descend the inside of a hopper, the upper bed part of contents (chip) maintaining the level surface,

it is useful for reduction of a raw material segregation. A more desirable angle of inclination is not less than 70 degrees. The angles of inclination of a hopper are a funnel-like oblique side and an angle between level line segments. It is good to use two or more hoppers upstream of the last hopper, and for not less than 65 degrees of angles of inclination to be not less than 70 degrees more preferably also in which hopper in this case.

[0076]

(3) Rationalization of hopper capacity

As a means to reduce the raw material segregation within a hopper, it is also a desirable means to rationalize the capacity of a hopper. As proper capacity of a hopper, it is within the limits of 15 – 120 mass % of the discharge quantity per hour of an extrusion machine. In that adequate supply of a raw material is difficult when there is no capacity beyond the 15 mass % grade of this discharge quantity in a hopper, and too large a hopper. It is a Reason for carrying out hopper capacity in a mentioned range that there is a possibility that a raw material chip mixture will cover a long time, and will stop in a hopper, and the segregation of a chip may arise in the meantime etc. The capacity of a hopper has more preferred within the limits of 20 – 100 mass % of the discharge quantity per hour of an extrusion machine.

[0077]

(4) Reduction of pulverized coal

in order to obtain a long film with a uniform presentation, the raw material chip to be used can be deleted -- etc. -- it is also a desirable means to reduce the ratio of the pulverized coal to generate. Since pulverized coal promotes generating of a raw material segregation, it is preferred to remove the pulverized coal generated within a process and to reduce the ratio of the pulverized coal contained in a hopper. As for the ratio of the pulverized coal contained, it is preferred to control in raw material 100 mass % and within 1 mass % through a whole process until a raw material chip goes into an extrusion machine, and controlling within 0.5 mass % is still more preferred. What is necessary is just to specifically remove pulverized coal by the method of letting a cyclone type air filter pass, when air feeding etc. carry out the method and raw material chip which let a screen pass, etc., after manufacturing a chip with a strand cutter.

[0078]

(5) Equalization of the skin temperature of the film in a stretching process

The process change at the time of extending a film other than the composition change of the polyester component which constitutes the above-mentioned film is also

mentioned to the factor which fluctuates the heat contraction action of a long film. That is, in order to reduce heat shrinkage rate change of a long film, it is preferred to deter the temperature change in the process of extending a film, and to reduce the range of fluctuation of the skin temperature of a film as much as possible.

[0079]

When extending one axis in a transverse direction using a tenter in the case of polyester film, there are the preheating process before extension, a stretching process, a heat treatment process after extension, relaxing treatment, a re-stretching treatment process, etc. Especially the thing that the range of fluctuation of the skin temperature of the film measured in an optional point controls in mean temperature of less than \*\*1 \*\* in a preheating process, a stretching process, and the heat treatment process after extension is a desirable means for equalization of a heat contraction action. It is still more desirable if it is less than \*\*0.5 \*\* in mean temperature.

[0080]

The temperature change in a preheating process, a stretching process, and the heat treatment process after extension affects greatly change of a heat shrinkage rate (a maximum shrinkage direction and direction crossing at a right angle) or a maximum-heat-shrinkage-stress value. Therefore, if the range of fluctuation of the skin temperature of the film in these processes is small, a film overall length will be covered, it will be extended and heat-treated at the same temperature, and a heat contraction action will equalize. Of course, also in relaxing treatment or a re-stretching treatment process, it is preferred that the range of fluctuation of the skin temperature of a film is small.

[0081]

Use the wind-speed-fluctuation control equipment which attached the inverter so that the wind speed of the hot wind which heats a film could be controlled, for example, in order to make change of film surface temperature small, or, It is good to use the equipment etc. which use low-pressure steam of 500 or less (below 5 kgf/cm<sup>2</sup>) kPa for a heat source, and can control the temperature change of a hot wind.

[0082]

The range of fluctuation of the skin temperature of the film measured in an optional point means the range of fluctuation at the time of measuring film surface temperature, for example with a non-contact infrared-type surface pyrometer continuously during film manufacture in the place which has passed 2 m after going into the stretching process, for example. Since the mean temperature is computable when the film manufacture for one roll is completed, if the range of fluctuation of film

surface temperature is less than \*\*1 \*\* in mean temperature, the overall length of the constant region of a film will be covered, it will be extended on the conditions, and change of a heat contraction action will also become small.

[0083]

In order to equalize the presentation of a long film and to suppress change of a heat contraction action, it is preferred to adopt all of above-mentioned means (1) – (5). Therefore, the angle of inclination of a means (2) using the raw material chip of the size which reduces pulverized coal and is specified for a means (1) by a means (4) at not less than 65 degrees. And it is desirable to perform a stretching process, where it produced the film and temperature controlling is precisely carried out by a means (5), carrying out constant feeding to an extrusion machine continuously, and controlling discharge quantity, after capacity mixes each raw material chip using the hopper with which it is satisfied of a means (3). A raw material chip may be supplied to the last hopper and an extrusion machine via some middle (buffer) hoppers, after mixing beforehand. When mixing two or more sorts of raw material chips, there are the method of mixing a priori using the method of mixing within a hopper using the device which can carry out constant feeding of the raw material chip continuously, or a blender, etc., but. In the case of the latter, it is preferred to care about a raw material chip size etc. so that a raw material segregation may not occur at the time of discharge of a mixture.

[0084]

The example of manufacture of concrete polyester film is explained. First, it dries using dryers, such as a hopper dryer and a paddle dryer, or a vacuum dryer, and the raw material chip controlled in the size with which it is satisfied of a means (1) is extruded to film state at the temperature of 200–300 \*\*. Or an undried polyester raw material is similarly extruded to film state, removing moisture within a vent type extruder. On the occasion of extrusion, a T-die method, a tubular method, etc. may adopt any existing method. It cools with a casting roll and after extrusion obtains an unstretched film (quenching). The film on which tension required for a film advance acted shall also be contained in this "unstretched film."

[0085]

Although the film which consists of a single layer as a film wound around the film roll of this invention may be sufficient, it may be the laminated film which laminated two or more layers (for example, two-layer, three layers, four etc. layers, etc.). When considering it as a laminated film, polyester of the same presentation as each class may be adopted, but it is also preferred to use polyester of a different presentation for

every layer. In the case where it is considered as three layers, a central layer is also recommended having composition using polyester of other presentations using polyester of the presentation same to both outer layers. Although the laminating method in particular in the case of considering it as such a laminated film is not limited, the method of obtaining the above-mentioned unstretched film is employable by the publicly known co-extruding method etc., for example.

[0086]

As mentioned above, an electrode is allocated between the above-mentioned extrusion machine and a casting roll, voltage is impressed between an electrode and a casting roll, and it is recommended also in that sticking a film on a roll electrostatically attains equalization of the thickness distribution of a film.

[0087]

Stretching treatment is performed to the above-mentioned unstretched film. After cooling by the above-mentioned casting roll etc., stretching treatment may be performed continuously, is once rolled round to rolled form after cooling, and is good in backward [ the ].

[0088]

In order to attain the purpose of this invention, since it is practical on productive efficiency that a maximum shrinkage direction is the direction of film width (width), it shows the example of the method of extending in the case of making a main shrinkage direction into a transverse direction hereafter. Also when making a maximum shrinkage direction into the direction of film length (straight side), changing 90 degrees etc. can extend the extension direction in the following method according to normal operation.

[0089]

If its attention is paid to making the thickness distribution of the target heat contraction nature polyester system film equalize, When extending in a transverse direction using a tenter etc., it is preferred to perform a preheating process in advance of a stretching process, and in this preheating process. It is preferred to heat until it reaches a certain temperature within the limits whose film surface temperature is  $T_g+0 **-T_g+60 **$  at a low wind speed so that thermal conductance may become in below  $0.00544 \text{ J/cm}^2, \text{ sec, and } ** (0.0013-\text{calorie/cm}^2, \text{ sec, and } **)$ .

[0090]

Lateral extension is performed with the prescribed temperature of  $T_g-20 **-T_g+40 **$  (preferably  $T_g-5 **-T_g+15 **$ ) within the limits. In order to satisfy said heat contraction characteristic, it is desirable to divide extension into two or more steps,

and to perform it. Hereafter, it explains taking the case of the case where it extends in two steps.

[0091]

The 1st step of extension is performed first. Draw magnification is preferably extended to 5.5 or less times 4.8 or more times 6.0 or less times 4.4 or more times. Draw magnification is preferably made into 5.5 or less times 4.8 or more times 6.0 or less times 4.4 or more times to an unstretched film. The 1st step of extension temperature is made into the above-mentioned temperature (prescribed temperature of  $T_g-5^{\circ}\text{C}$  to  $T_g+15^{\circ}\text{C}$  within the limits).

[0092]

Next, it is preferred to perform heat setting, where a film is strained in the extension direction. Making the stress rate in that case into 5% or less not less than 2% preferably 6% or less 1% or more to the film after the 1st step of extensions is recommended. Heat setting temperature carries out [ about  $1-5^{\circ}\text{C}$  / temperature / the 1st step of / extension ] whether it is made the same as the 1st step of extension temperature in the above-mentioned temperature requirement, and, as for heat setting time, it is desirable for 3 or less seconds to take 1 second or more preferably 5 or less seconds 0.5 second or more.

[0093]

Next, the 2nd step of extensions are performed. Draw magnification is made into 1.5 or less (preferably 1.3 or less times) times 1.1 or more times to the film after heat setting (after [ when not carrying out heat setting ] the 1st step of extensions). As for the 2nd step of extension temperature, it is preferred to carry out [ about  $1-5^{\circ}\text{C}$  / temperature / heat setting ] whether it is made the same as heat setting temperature in the above-mentioned temperature requirement.

[0094]

Then, applying stress slightly [ it is desirable and ] on a film, it cools and a heat contraction nature polyester system film is obtained. As for the stress rate at the time of cooling, it is preferred to consider it as 0.1 to 3% to the film after the 2nd step of extensions.

[0095]

When making the process of extension into a three-stage, it is desirable to put in the above-mentioned heat setting process between the 2nd step of extensions and extension of a three-stage eye. What is necessary is just to determine the conditions of a heat setting process according to the above-mentioned heat setting conditions. What is necessary is just to also determine the extension conditions of a three-stage

eye according to the 2nd step of above-mentioned extension conditions.

[0096]

Since the design of the extension equipment in industrial production becomes difficult from viewpoints of heat shrinkage rate control of a film, etc. when there are not much too many step numbers although more ones of the step number of extension are preferred, it is desirable to consider it as four or less steps preferably six or less steps.

[0097]

In this lateral orientation process, it is preferred to use the equipment which can make change of film surface temperature small, as described above.

[0098]

As the method of extension, 1.1 times – 2.0 times as many extensions may be preferably given to not only the width 1 axis extension by a tenter but a lengthwise direction 1.0 time – 4.0 times. Thus, when performing biaxial extension, any of biaxial extension and simultaneous biaxial extension may be sufficient one by one, and re-extension may be performed if needed. In biaxial extension, which methods, such as every direction, length-and-breadth, in every direction length, and length-and-breadth width, may be used as an order of extension one by one. Also in the case where these vertical stretching processes or a biaxial stretching process is adopted, it is preferred like lateral orientation to make change of film surface temperature as small as possible in a preheating process, a stretching process, etc.

[0099]

As for the coefficient of heat transfer of a stretching process, if the point which controls internal generation of heat of the film accompanying extension, and makes crosswise film temperature spots small is noted, it is preferred to use more than 0.00377 J/cm<sup>2</sup>, sec, and \*\* (0.0009–calorie/cm<sup>2</sup>, sec, and\*\*). 0.00544 – 0.00837 J/cm<sup>2</sup>, sec, and \*\* (0.0013–0.0020–calorie/cm<sup>2</sup>, sec, and\*\*) are more preferred.

[0100]

As for the heat contraction nature polyester system film roll in this invention, it is preferred to roll round a 0.2 m or more-wide heat contraction nature polyester system film, and to roll round not less than 300 m in length to a core (core). The utility value of the roll of a film with which width is less than 0.2 m is industrially low, and since there is little volume length of a film and the presentation covering the overall length of a film and change of a heat contraction action become small, the effect of this invention becomes difficult to reveal the film roll which is less than 300 m in length. As for the width of a heat contraction nature polyester system film roll, 0.3 m or more is more preferred, and its 0.4 m or more is still more preferred. As for the length of the heat

contraction nature polyester system film wound around a roll, not less than 400 m is more preferred, and its not less than 500 m is still more preferred.

[0101]

As for 1.5 m or less in width, and volume length, in the case of 45-micrometer film thickness, generally, 6000 m or less is preferred, although the width of a film roll and the maximum in particular of volume length are not restricted from the ease of carrying out of handling. As a rolling-up core, plastic cores, such as 3 inches, 6 inches, and 8 inches, a metal core, or a paper tube can usually be used.

[0102]

Although the thickness in particular of the film which constitutes the heat contraction nature polyester system film roll of this invention is not limited, for example as a heat contraction nature polyester system film for labels, 10–200 micrometers is preferred, 20–100 micrometers is more preferred, and 20–60 micrometers is still more preferred.

[0103]

Even if it uses the heat contraction nature label obtained using the heat contraction nature polyester system film wound around the roll of this invention for full labels (label that high contraction is required selectively), such as a PET bottle, it can present good contraction result appearance. It can become high contraction by short-time processing. It also has the effect of reinforcing containers, such as a PET bottle by which covering contraction was carried out. There is no dispersion in the heat contraction action of one-piece one label, and a poor incidence rate is very small.

[0104]

In order to use the above-mentioned heat contraction nature polyester system film as a heat contraction nature label, For example, letting [ after carrying out predetermined time storage into the environment which controlled temperature and humidity, take out the heat contraction nature film roll before contraction, and ] out a film from a roll. Using publicly known tube shape molding equipment, a film is rounded off promptly, and an end is piled up, and it pastes [ the solvent for adhesion is applied inside with prescribed width for a while from the edge of one side of a film piece end, and ] up, and is processed into a tube. The processed tube can be wound around a roll in the state where it once crushed level, or can be continuously cut out to predetermined length after tube processing, and can be used as a heat contraction nature label.

[0105]

As for adhesion of a film, although it is also possible to adopt the melt adhesion method to which melting of a part of film is carried out, it is preferred to carry out from a viewpoint of controlling change of the heat contraction characteristic of a label,

etc., using a solvent. As a solvent which can be used, for example Benzene, toluene, xylene, Aromatic hydrocarbon, such as trimethyl benzene; although organic solvents, such as oxo orchid species [, such as franc;1,3-dioxolanes, such as phenols; tetrahydrofurans, such as halogenated hydrocarbon; phenol such as a methylene chloride and chloroform, ]; are mentioned, Especially, 1,3-dioxolane is desirable at the point that safety is high.

[0106]

After equipping containers, such as a PET bottle, with the above-mentioned heat contraction nature label, heat contraction of it can be carried out by publicly known heat contraction means (a hot wind tunnel, a steam tunnel, etc.) which were mentioned above.

[0107]

Even if weight is about 30% lower than the conventional PET bottle, the PET bottle which carried out covering contraction of the heat contraction nature label of this invention is reinforced, for example to such an extent that it can be dealt with like the conventional PET bottle, for example in the cases, such as transportation and sale. It is preferred that not less than 75% of the drum section surface area of a PET bottle is covered with the label in this case.

[0108]

For example, in the label produced from the heat contraction nature film of this invention by performing it as follows, preferably, the diameter rate of change of a bottle measured by the after-mentioned method is 7% or less more preferably, and can demonstrate the outstanding container reinforcing effect 10% or less.

[0109]

After applying 1,3-dioxolane inside by 3\*\*1-mm width for a while from the edge of one side of one end of a film (coverage: 3.0\*\*0.3g/mm<sup>2</sup>) and piling up this end, it judges in 14 cm in length, and size 6.7 cm in diameter, and a cylindrical label is obtained. It seals, after filling up a 500mL round shape PET bottle [21 cm in height, and center-section (drum section) 6.5 cm in diameter] with a mass of 20.5 g with the water of 500mL, and this is equipped with the above-mentioned cylindrical label, a steam tunnel with a zone temperature of 85 \*\* is passed in 2.5 seconds, and this label is shrunk. Thus, the path (W<sub>1</sub>) of a bottle center section when "straw graph V10-C" by an Oriental energy machine company is used for the side center section of the label covering bottle obtained and 15 kg of load is imposed on it by compressed mode is measured, and the diameter rate of change of a bottle (%) is searched for according to a following formula.

Diameter rate of change of a bottle (%) =100x(W<sub>1</sub>-W<sub>2</sub>)/W<sub>2</sub>

Here,  $W_2$  is a path of the bottle center section before imposing load.

[0110]

Since it is easy to transform this container and may become causes, such as plugging, in the label that the above-mentioned diameter rate of change of a bottle exceeds 10% when a covering container falls, for example within a vending machine, it is not desirable.

[Example]

[0111]

Although this invention is further explained in full detail according to working example below, following working example does not restrict this invention, and when carrying out change implementation in the range which does not deviate from the meaning of this invention, it is included in this invention. The measuring method of the physical properties of the film obtained by working example and a comparative example is as follows.

[0112]

(1) The check of a constant region, and setting out of a sample logging part

About the film roll around which the film with a length of 1000 m obtained by working example and the comparative example which are mentioned later was wound. A five-point sample was started at intervals of 20 m from the 2nd end (winding end part) of the film, the sample of five points was started at intervals of 20 m towards said 1st end from the portion of the 1st end (cut-water part) of a film to the 200-m inside, and the heat shrinkage rate (after-mentioned) of the maximum shrinkage direction of these samples was measured. The heat shrinkage rate of each sample was settled in less than 20% of width. And manufacture and a stretching process were stable during manufacture of a film. Therefore, each film roll covering the overall length of a film, and corresponding to the constant region was checked.

[0113]

In each measurement, the 1st sample logging part was used as the 2nd end (from the end of a volume to 0 m) of a film, and the last sample logging part considered it as the 1st end (from a cut water to 0 m) of the film, and extracted the sample from 11 sample logging parts in all. Unless it refused especially in each physical-properties measurement, ten samples were started from each sample logging part, and the average value of the physical properties of ten samples in each sample logging part was made into the property value of the sample in the logging part.

[0114]

(2) Heat shrinkage rate

A film is judged in square of 10 cm x 10 cm in each above-mentioned sample logging part, After being immersed for 5 seconds and carrying out heat contraction by no load condition into the warm water of the temperature of following (A), (B), and (C), it is made to be immersed in 25 \*\* underwater [ \*\*0.5 \*\* ] for 10 seconds, and it pulls out from this underwater one, the length of a sample and lateral length are measured, and it asks according to a following formula.

Heat shrinkage rate (%) =  $100 \times (\text{length after contraction} - \text{length before contraction}) / (\text{length before contraction})$

Here, they are (A):75 \*\*\*\*0.5 \*\*, (B):85 \*\*\*\*0.5 \*\*, and (C):95\*\*0.5 \*\*. Let the direction which intersects a direction with the largest contraction perpendicularly with a maximum shrinkage direction and a maximum shrinkage direction be direction crossing at a right angle. In the temperature of the above (B), the average value, the maximum, and the minimum of the heat shrinkage rate in all the films were shown in Table 4. The average value, the maximum, and the minimum of the heat shrinkage rate were shown [ film No.2, and / 9 and 11 ] in Table 5 also about the temperature of (A) and (C). The heat shrinkage rate about other films showed only the average value of all the samples in Table 4 and Table 6.

[0115]

### (3) Heat shrinkage rate difference delta

The mold which counters and has two zippers is prepared so that only the end of the lot which a rectangular film counters can be grasped. A heat contraction nature polyester system film is judged in a square or a rectangle in parallel with a maximum shrinkage direction. The film after decision is fixed with a described [ above ] type. Immobilization is performed by slackening a film so that the both ends which intersect perpendicularly with the maximum shrinkage direction of this film may be grasped by a zipper and the film length between zippers and the ratio of the distance between zippers of a mold may be set to 1:0.9. Then, after immersing the film fixed to the mold for 5 seconds and carrying out heat contraction by no load condition into 95 \*\* \*\*0.5 \*\* warm water, promptly, by no load condition, it is immersed for 10 seconds in 25 \*\* underwater [ \*\*0.5 \*\* ], and pulls up to it. This film is removed from a mold, attached groundwater is removed, and the film made [ the maximum shrinkage direction ] to carry out heat contraction 10% is obtained. Then, in the state of an atony, this film is placed in the air and under the environment of 25 \*\* or less, and the following process is presented as much as possible with it for a short time.

[0116]

Judge this film in square of 10 cm x 10 cm, and in 95\*\*0.5 \*\* warm water, After being

immersed for 5 seconds and carrying out heat contraction by no load condition, it is made to be immersed in 25 \*\* underwater [ \*\*0.5 \*\* ] for 10 seconds, and it pulls out from this underwater one, the length of a sample and lateral length are measured, and it asks for heat shrinkage rate  $X_{10}$  of a maximum shrinkage direction according to the above-mentioned heat shrinkage rate formula. The heat shrinkage rate of the maximum shrinkage direction called for on condition of (C) of the above (1) is made into  $X_0$ . From these values, according to the lower type, the heat shrinkage rate difference delta (%) was computed, and the average value about all the samples was shown in Tables 4 and 6.

$$\text{delta} = X_0 - X_{10}$$

[0117]

#### (4) Maximum-heat-shrinkage-stress value

It measures using a tension tester with a heating furnace (the "tensilon" by Oriental energy machine incorporated company). From the film before heat contraction, at 200 mm, start a 20-mm-wide sample, and the length of a maximum shrinkage direction stops air blasting of the tension tester beforehand heated at 90 \*\*, makes a sample the distance between zippers of 100 mm, and it The length between zippers of a specimen, After the distance between zippers slacks a specimen and attaches it so that it may be set to 1:0.9, The door of a heating furnace is shut promptly, the contraction stress detected in a 5 m [ in (temperature of 90 \*\* and blow-off speed ]/second hot wind when supply) is started from the three way of the back, the left, and the right is measured, and the maximum-heat-shrinkage-stress value (MPa) after 10% contraction is calculated from a measurement chart. The average value of the maximum-heat-shrinkage-stress value of all the samples was shown in the table in Table 6.

[0118]

#### (5) Thickness distribution

Ten specimens which make the maximum shrinkage direction of a film the length direction are created for every logging part at 50 cm in length, and 5 cm in width, About each specimen, contact process thickness meters, such as for example, "KG60/A" (by ANRITSU CORP. etc.), are used, After measuring the thickness of the length direction continuously, outputting to a chart, asking for maximum thickness, the minimum thickness, and average thickness from this output and computing thickness distribution using a lower type from these, the average value of the thickness distribution of ten specimens is made into the thickness distribution of the film in the logging part. The average value of the thickness distribution in all the logging parts was

shown in the table in Table 6.

Thickness distribution = [(the maximum thickness–minimum thickness) / average thickness] x100

[0119]

(6) Melt resistivity value

The electrode plate of a couple is inserted into the sample (film) fused at the temperature of 275 \*\*, and the voltage of 120V is impressed. The current in that case is measured and melt resistivity value Si (ohm–cm) is computed based on a lower type. The average value of the melt resistivity value in all the logging parts was shown in Table 6.

$$Si = (A/I) \times (V/io)$$

here -- area [ of A:electrode ] (cm<sup>2</sup>), and I:inter electrode distance (cm) V:voltage (V), and io: -- it is current (A).

[0120]

(7) Contraction result nature

A film overall length is covered, 3 color prints are carried out in the green by TOYO INK MFG. CO., LTD., and golden and white ink, and it once scrapes off, and is kept for 250 hours in the environment controlled to the temperature of 30\*\*1 \*\*, and 85\*\*2% of relative humidity. Then, 1,3-dioxolane is applied inside by 3\*\*1-mm width for a while from the edge of one side of one end of a film using tube shape molding equipment (coverage: 3.0\*\*0.3g/mm<sup>2</sup>), A film is rounded off promptly, and an end is piled up, and it pastes up, is considered as a tube, and rolls round in the state where it crushed level. This tube is cut out and it is considered as a cylindrical label 14 cm in height, and 6.7 cm in diameter. 500mL round shape PET bottle [21 cm in height which created five labels in each above mentioned sample logging part, and were made to fill up a label with water. Center-section (drum section) 6.5–cm] is equipped, the label whole quantity is passed for under the steam tunnel by FUJI ASTEC Co., Ltd.

(SH-1500-L) on conditions with a zone temperature of 85 \*\* for tunnel pass time 2.5 seconds, and a label is shrunk. [ in diameter ] The grade of the contraction result was judged visually, contraction result nature was evaluated in two steps, and it was shown in Table 6. In O:wrinkles, a jump, and the shortage of contraction, generating nothing, x:wrinkles, a jump, or the shortage of contraction used the standard as every label with generating at one or more labels.

[0121]

(8) Container reinforcing effect (diameter rate of change of a bottle)

A tube roll is produced like the time of evaluation of contraction result nature. This

tube is cut out and it is considered as a cylindrical label 14 cm in height, and 6.7 cm in diameter. Mass : It seals, after filling up a 20.5-g 500mL round shape PET bottle [21 cm in height, and center-section (drum section) 6.5 cm in diameter] with the water of 500mL, This is equipped with the above-mentioned cylindrical label, the label whole quantity is passed for under the steam tunnel by FUJI ASTEC Co., Ltd. (SH-1500-L) on conditions with a zone temperature of 85 \*\* for tunnel pass time 2.5 seconds after that, and a label is shrunk.

[0122]

Thus, the path ( $W_1$ ) of a bottle center section when "straw graph V10-C" by an Oriental energy machine company is used for the side center section of the label covering bottle obtained and 15 kg of load is imposed on it by compressed mode is measured, and the diameter rate of change of a bottle (%) is searched for according to a following formula.

$$\text{Diameter rate of change of a bottle (\%)} = 100 \times (W_1 - W_2) / W_2$$

Here,  $W_2$  is a path of the bottle center section before imposing load.

[0123]

The synthetic example 1 (composition of polyester)

With an esterification reaction can, as polyvalent carboxylic acid, dimethyl terephthalate (DMT) 100 mol %, As a polyhydric alcohol class, ethylene glycol (EG) 100-mol %, Teach by 2.2 times (mole ratio) to polyvalent carboxylic acid, and as a catalyst antimonous oxide, It taught simultaneously, and temperature up was carried out to 230 \*\*, agitating, and the ester exchange reaction was performed by ordinary pressure for 120 minutes so that it might be set to 81 ppm by Mg atom conversion to the polyester which has 0.04-mol % and magnesium acetate 4 hydrate formed to polyvalent carboxylic acid. The end of the ester exchange reaction was considered as the place which methanol of the specified quantity distilled off. The polycondensation reaction was performed for about 40 minutes, and the polyester A was obtained after the end of an ester exchange reaction until a temperature raising and melt viscosity became 7000 poise to 280 \*\*, decompressing [ added so that it might be set to 58 ppm to the polyester formed by P atom conversion, and ] trimethyl phosphate over 85 minutes. The intrinsic viscosity of this polyester A was 0.75 dl/g. After a polymerization, by a molten state, the obtained polyester is picked out from a polymerization apparatus by strand shape, and is water-cooled promptly. Then, it cut with the strand cutter and the raw material chip A was obtained.

[0124]

Intrinsic viscosity is the value measured at 30\*\*0.1 \*\* with the Ostwald viscometer, after weighing the chip 0.1g precisely and dissolving in the 25-ml mixed solvent of phenol/tetrachloroethane =3 / 2 (mass ratio).

[0125]

The synthetic examples 2-8

By the same method as the synthetic example 1, polyester raw material chip B-H was obtained by the preparation presentation shown in Table 1. In the synthetic examples 2 and 3, as a polymerization catalyst, antimonous oxide was used so that Sb atoms might be set to 160 ppm to polyester, and the polyester B and C was obtained. In the synthetic examples 4 and 8, as a polymerization catalyst, titanium tetrabutoxide was used so that Ti atoms might be set to 90 ppm to polyester, and the polyester D was obtained. Furthermore, in the synthetic example 6, cobaltous acetate 4 hydrate is made for Mg atom to be set to 20 ppm to polyester as a polymerization catalyst, further, titanium tetrabutoxide was used so that Ti atoms might be set to 15 ppm to polyester, and the polyester F was obtained. In the synthetic examples 5 and 7, it was presupposed about the polymerization catalyst that it is the same as that of the synthetic example 1. The chip D and the chip H change the cut conditions of a chip with the same polyester. The chip H is a small chip for comparative examples. As for ethylene glycol and NPG, dimethyl terephthalate and DMN are [ DMT / dimethyl naphthalate and EG / 1,4-butanediol and CHDM of neopentyl glycol and BD ] 1,4-cyclohexane dimethanol among front, and PPG is a brief sketch of a propanediol.

[0126]

Working example 1

As predrying of each chip obtained in the above-mentioned synthetic example is carried out separately and it was shown in Table 2, Supplying the chip A by 15 mass %, and supplying continuously the chip D of 75 mass % and 10 mass % for the chip B to the hopper of extrusion machine right above independently with a screw feeder in fixed quantity. It mixed within this hopper, melt extruding was carried out with the monopodium type extrusion machine at 280 \*\*, it quenched after that, and the 260-micrometer-thick unstretched film was obtained. The shape difference (%) over the chip B with most amount used was combined with Table 2, and was shown. The hopper has the capacity containing 150 kg of raw material chips.

The discharge quantity of the extrusion machine was 450 kg per hour.

The angle of inclination of the hopper was 70 degrees.

[0127]

After preheating the above-mentioned unstretched film for 3 seconds at 100 \*\*, carry

out extension (the 1st step) to a transverse direction 4.75 times at 77 \*\* by a tenter, subsequently make it become it tense by 77 \*\* 3% to the film width at the time of the end of the 1st step for 5 seconds (heat setting), and, subsequently at 75 \*\*. It carried out by extending by 1.1 times the film width at the time of the end of heat setting (the 2nd step). Subsequently, it cools to the film width at the time of the 2nd step of ends of extension, applying 1% of stress, and it continues for not less than 1000 m in length, a 50-micrometer-thick polyester system film is produced continuously, and it wound around roll No.1. Here, in working example 1, the range of fluctuation of film surface temperature when continuous fabrication of the film is carried out was [ in the preheating process ] within the limits with a mean temperature of \*\*0.5 \*\* in the mean temperature of \*\*0.6 \*\*, and a heat treatment process at the mean temperature of \*\*0.8 \*\*, and a stretching process. The skin temperature of the film was measured using the non-contact infrared-type surface pyrometer (it is the same also at the following working example and a comparative example). The evaluation result of the obtained film roll is shown in Tables 4-6.

[0128]

Working example 2

Heat contraction nature polyester system film roll No.2 was obtained like working example 1 except having changed the kind and quantity of the chip which were used, as shown in Table 2, and having changed extension conditions using the hopper whose angle of inclination is 75 degrees, as shown in Table 3. The evaluation result of the obtained film roll is shown in Tables 4-6.

[0129]

Working example 3-7

Heat contraction nature polyester system film roll No.3 – 7 were obtained like working example 1 except having changed the kind and quantity of the chip which were used, as shown in Table 2, and having changed extension conditions, as shown in Table 3. The evaluation result of the obtained film roll is shown in Tables 4-6.

[0130]

Working example 8

Lamination polyester system film roll No[ of three layers ].8 which consists of both outer layers and a central layer was produced. The chip of 75 mass % and the polyester D was mixed for the chip of 15 mass % and the polyester C in the central layer at a rate of 10 mass %, and the chip of the polyester A which carried out predrying separately, respectively was used for it. The chip of 15 mass % and the polyester F was mixed in both outer layers at a rate of 85 mass %, and the chip of the

polyester A which carried out predrying separately, respectively was used for them. These mixed polyester chips were quenched with the casting roll a co-extrusion and after that at 280 \*\* using the single screw extruder which has a T die, and the thickness of both outer layers obtained the unstretched film of the three-tiered structure whose thickness of 65 micrometers and a central layer is 130 micrometers, respectively. About this unstretched film, it changed into the conditions shown in Table 3, and also extended like the experiment 1, and 50 micrometers (in thickness of both outer layers, thickness of 12.5-micrometer and central layer is 25 micrometers, respectively)–thick lamination polyester system film roll No.8 was obtained. The evaluation result of the obtained film roll is shown in Tables 4 and 6.

[0131]

Comparative example 1

It is the combination shown in Table 2, namely, chip A40 mass %, chip C50 mass %, and chip D10 mass % were mixed a priori, and predrying was carried out after that. 400 kg of raw material chips enter, and the angle of inclination of a hopper arranges in three-piece series the hopper of the same shape that is 60 degrees, and puts a chip mixture into an upstream hopper most. The 50-micrometer-thick heat contraction nature polyester system film obtained heat contraction nature film roll No.9 wound 1000m like working example 1 except having made it move to the 2nd piece and each 3rd (last hopper) hopper. The evaluation result of the obtained film roll is shown in Tables 4–6.

[0132]

Comparative example 2

The 200-micrometer-thick unstretched film was obtained like working example 1. After preheating this unstretched film for 10 seconds at 100 \*\*, by a tenter, carry out extension (the 1st step) to a transverse direction 3.64 times at 78 \*\*, and, subsequently at 78 \*\*. It extends 1.1 times to the film width at the time of the end of the 1st step (the 2nd step), and it continues for not less than 1000 m in length, a 50-micrometer-thick polyester system film is produced continuously, and it wound around roll No.10. In this comparative example 2, the range of fluctuation of film surface temperature when continuous fabrication of the film is carried out was [ in the preheating process ] within the limits with a mean temperature of \*\*2.0 \*\* in the mean temperature of \*\*2.5 \*\*, and a heat treatment process at the mean temperature of \*\*1.0 \*\*, and a stretching process. The evaluation result of the obtained film roll is shown in Tables 4–6.

[0133]

### Comparative example 3

It is the combination shown in Table 2, namely, chip A15 mass %, chip B75 mass %, and chip H10 mass % were mixed a priori, and predrying was carried out after that. 400 kg of raw material chips enter, and the angle of inclination of a hopper arranges in three-piece series the hopper of the same shape that is 60 degrees, and puts a chip mixture into an upstream hopper most, The 50-micrometer-thick heat contraction nature polyester system film obtained heat contraction nature film roll No.11 wound 1000m like working example 1 except having made it move to the 2nd piece and each 3rd (last hopper) hopper. The evaluation result of the obtained film roll is shown in Tables 4-6.

[0134]

[Table 1]

ポリエステル	仕込み組成						形状(平均値)(mm)			
	多価カルボン酸類(モル%)						多価アルコール類(モル%)			
	DMT	DMN	EG	NPG	BD	CHDM	PPG	断面長径	断面短径	チップ長さ
A	100	—	100	—	—	—	—	3.9	2.6	3.8
B	100	—	60	40	—	—	—	3.5	2.6	4.1
C	100	—	70	30	—	—	—	3.4	2.7	4.1
D	100	—	—	—	100	—	—	3.6	2.9	3.6
E	—	100	100	—	—	—	—	3.8	2.6	3.8
F	100	—	70	—	—	30	—	3.5	2.6	4.0
G	100	—	—	—	—	—	100	3.6	2.8	3.6
H	100	—	—	—	—	100	—	—	2.7	2.0

[0135]

[Table 2]

フィルム ローラNo.	層構成	ポリエチル混合組成(質量%)						原料チップの平均形状差(%)					
		A	B	C	D	E	F	G	H	断面長径	断面短径	チップ長さ	
No. 1	単層	15	75	—	10	—	—	—	—	11.4	11.5	-12.2	
No. 2	単層	10	80	—	10	—	—	—	—	11.4	11.5	-12.2	
No. 3	単層	15	80	—	5	—	—	—	—	11.4	11.5	-12.2	
No. 4	単層	15	—	75	10	—	—	—	—	14.7	7.4	-12.2	
No. 5	単層	—	—	—	15	85	—	—	—	—	—5.3	11.5	-5.3
No. 6	単層	15	—	—	—	—	85	—	—	11.4	0	-5.0	
No. 7	単層	15	—	75	—	—	—	10	—	11.4	7.7	12.2	
No. 8	3層積層	中心層	15	—	75	10	—	—	—	14.7	7.4	-12.2	
			15	—	—	—	—	85	—	11.4	0	-5.0	
No. 9	単層	40	—	50	10	—	—	—	—	11.4	11.5	-12.2	
No. 10	単層	15	75	—	10	—	—	—	—	11.4	11.5	-12.2	
No. 11	単層	15	75	—	—	—	—	—	10	21.0	21.5	21.0	

[0136]

[Table 3]

フィルム ロールNo.	ホッパの 傾斜角 (°)	延伸1段階目			熱固定			延伸2段階目			冷却時の 緊張率 (%)
		倍率 (倍)	温度 (°C)	緊張率 (%)	温度 (°C)	時間 (秒)	倍率 (倍)	温度 (°C)	倍率 (倍)	温度 (°C)	
No. 1	70	4.75	77	3	77	5	1.1	75	1	1	
No. 2	75	4.75	77	3	77	5	1.1	75	1	1	
No. 3	70	4.75	80	3	80	5	1.1	78	1	1	
No. 4	70	4.75	78	0	—	—	1.1	78	0	0	
No. 5	70	4.75	95	3	75	5	1.1	75	1	1	
No. 6	70	4.75	80	3	75	5	1.1	75	1	1	
No. 7	70	4.75	77	3	77	5	1.1	75	1	1	
No. 8	70	4.75	78	3	75	5	1.1	75	1	1	
No. 9	60	4.75	84	0	—	—	1.1	77	0	0	
No. 10	70	3.64	78	0	—	—	1.1	78	0	0	
No. 11	60	4.75	77	3	77	5	1.1	75	1	1	

[0137]

[Table 4]

フィルム ロールNo.	熱収縮率(%)			熱収縮率(B) 最大収縮方向(%)			
	(A) 70°C	(B) 85°C	(C) 95°C での△ Y	平均値 (X)	最大値 (Ymax)	最小値 (Ymin)	Ymax-X Ymin-X
No. 1	30	78	-1	10	78.0	79.0	77.0 1.0 1.0
No. 2	43	78	-3	11	78.0	79.0	77.0 1.0 1.0
No. 3	48	78	-3	11	78.0	79.0	77.0 1.0 1.0
No. 4	30	76	-2	15	76.3	77.5	75.3 1.2 1.0
No. 5	15	76	2	15	76.0	77.3	75.3 1.3 0.7
No. 6	13	76	-1	16	76.0	77.0	75.3 1.0 0.7
No. 7	42	77	1	11	77.0	78.0	76.0 1.0 1.0
No. 8	45	78	0	10	78.0	79.0	77.0 1.0 1.0
No. 9	20	69	1	30	68.8	74.3	61.8 5.5 7.0
No. 10	17	69	8	26	69.2	74.5	63.0 5.3 6.2
No. 11	31	78	-1	11	78.0	79.0	72.5 1.0 5.5

[0138]

[Table 5]

フィルム ロールNo.	熱収縮率(A) 最大収縮方向(%)				熱収縮率差Δ(C)(%)			
	平均値 (X)	最大値 (Ymax)	最小値 (Ymin)	Ymax-X	Ymin-X	平均値 (X)	最大値 (Ymax)	最小値 (Ymin)
No. 2	43.0	45.5	40.0	2.5	3.0	11.0	12.0	10.0
No. 9	20.0	26.0	13.5	6.0	6.5	30.0	36.0	26.5
No. 11	31.0	36.5	24.0	5.5	6.0	11.0	21.0	10.0

[0139]

[Table 6]

フィルム ロールNo.	熱収縮率(%)			最大 熱収縮 応力値 (MPa)	収縮 仕上り性	厚み分布 (%)	溶融 比抵抗値 ( $\times 10^8$ $\Omega \cdot \text{cm}$ )	ボトル径 変化率 (%)
	(A) 70°C 最大収縮 方向	(B) 85°C 最大収縮 方向	(C) 95°C での $\Delta$					
No. 1	30	78	-1	10	12	○	0.8	0.32
No. 2	43	78	-3	11	12	○	0.9	0.27
No. 3	48	78	-3	11	14	○	0.7	0.31
No. 4	30	76	-2	15	8	○	1.3	0.32
No. 5	15	76	2	15	10	○	1.0	0.65
No. 6	13	76	-1	16	14	○	0.9	0.31
No. 7	42	77	1	11	11	○	1.1	0.41
No. 8	45	78	0	10	12	○	1.0	0.32
No. 9	20	69	1	30	5	×	2.0	0.55
No. 10	17	69	8	26	4	×	2.5	0.32
No. 11	31	78	-1	11	12	×	1.5	0.32

[0140]

It turns out that it is made to go via two or more hoppers with a small angle of

inclination, or a raw material segregation happens in the comparative examples 1 and 3 (roll No.9 and 11) which manufactured the long film using the small chip H for comparative examples, and the heat shrinkage rate varies so that clearly from Table 1 – 6. As a result, the defect had occurred by contraction result nature. Dispersion in a heat shrinkage rate was seen also in the comparative example 2 (roll No.10) which did not perform temperature control in the stretching process strictly. Since the chip to which it was equal in size in working example on the other hand was used, a raw material segregation did not happen, but dispersion in the heat contraction characteristic was not accepted, but each property value was also good.